Optical and Quantum Electronics **34:** 71–77, 2002.
© 2002 *Kluwer Academic Publishers. Printed in the Netherlands.*

Introducing CdS into two- and three-dimensional photonic crystals

OSAMU HANAIZUMI[1]*†, MAKOTO SAITO[1], YASUO OHTERA[1], SHOJIRO KAWAKAMI[2], SATOSHI YANO[3], YUSABURO SEGAWA[3], EIICHI KURAMOCHI[4], TOSHIAKI TAMAMURA[4], SATOSHI OKU[5] AND AKIRA OZAWA[6]

[1]*Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan;*

[2]*New Industry Creation Hatchery Center, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan;*

[3]*Photodynamics Research Center, The Institute of Physical and Chemical Research, 19-1399 Koeji, Nagamachi, Aoba-ku, Sendai 980-0868, Japan;*

[4]*NTT Basic Research Laboratories, 3-1 Morinosato-Wakamiya, Atsugi 243-0198, Japan;*

[5]*NTT Photonics Laboratories, 3-1 Morinosato-Wakamiya, Atsugi 243-0198, Japan;*

[6]*NTT Advance Technology, 3-1 Morinosato-Wakamiya, Atsugi 243-0198, Japan*

*(*author for correspondence, E-mail: hana@el.gunma-u.ac.jp)*

(†Present address: Department of Electronic Engineering, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-Cho, Kiryu 376-8515, Japan)

Abstract. SiO_2/air three-dimensional (3D) periodic structures were fabricated by removing Si layers partially from Si/SiO_2 3D photonic crystals (PhCs) formed by using autocloning. CdS/SiO_2 3D periodic structures were formed by introducing CdS into the SiO_2/air structures by the TEA method and photoluminescence (PL) was observed from the introduced CdS. TiO_2/air/CdS two-dimensional (2D) PhCs were also fabricated by introducing CdS into the voids of TiO_2/air 2D periodic structures, in which SiO_2 layers were partially etched out from TiO_2/SiO_2 2D PhCs fabricated by using autocloning. PL radiating normal to the surface was measured and large polarization dependence was observed.

Key words: autocloning, Cds, photoluminescence, photonic crystal, TEA method

1. Introduction

Photonic crystals (PhCs) have a photonic band gap, a large anisotropy and high dispersion, and so they could potentially be used to create novel devices. Flexibility and controllability of PhCs can be greatly improved by using the autocloning technology we have previously proposed (Kawakami 1997). Polarization splitters (Ohtera *et al.* 1999), superprism effect (Kosaka *et al.* 1998), and surface-normal optical waveguides (Hanaizumi *et al.* 1999) have already been demonstrated. In addition, PhCs composed of active materials can be used to produce zero-threshold lasers utilizing the photonic band gap effect in the stopband, and this has been one of the major device applications of PhCs since this concept was proposed (Yablonovitch 1987). Because PhCs

have a large anisotropy and high dispersion in the passband, things such as luminescent devices radiating light at only a certain polarization can be made from them. Laser oscillation achieved by combining active materials and two-dimensional (2D) PhCs has been reported (Inoue *et al.* 1998; Imada *et al.* 1999; Meier *et al.* 1999; Painter *et al.* 1999). For three-dimensional (3D) structures, however, only basic experiments using synthetic opals have been reported (Romanov *et al.* 1998; Yoshino *et al.* 1998). In this paper, we demonstrate the process of introducing CdS into 3D periodic structures, which is the first step in using PhCs to create luminescent devices with excellent polarization controllability and connectivity with waveguides. Photoluminescence (PL) was observed to result from the introduction of CdS. TiO_2/air/CdS 2D PhCs were also successfully fabricated, and the suppression of a certain polarization of PL was observed.

2. Introducing CdS into 3D PhCs

2.1. FABRICATION PROCESS

Our method for introducing CdS into 3D PhCs was as follows

(1) Periodic circular pits with a triangular lattice configuration were formed on an InP substrate by electron beam (EB) lithography and dry etching. The center-to-center distance of pits was 0.5 μm. Luminescence from the back side of the substrate was not needed in our experiments, so we chose InP as the substrate, because it is easy to cleave.
(2) Alternating multilayers of Si/SiO_2 were deposited by rf bias sputtering (20 periods). The thickness of each layer was 0.3 μm, and the total thickness was 12 μm.
(3) Rectangular holes of $3 \times 9 \times 12$ μm^3 were formed using focused ion beam (FIB) etching.
(4) SiO_2/air 3D periodic structures were formed 5 μm depth from the walls of the rectangular holes, by selective etching of Si layers using KOH etchant.
(5) CdS was introduced into the air region by the TEA method (Hu and Nair 1995). In order to obtain a higher intensity of luminescence, we changed the mixture ratio to $Cd(NO_3)_2$:NH_4OH:$SC(NH_2)_2$:$N(CH_2CH_2OH)_3$ = 1:14.4:1:3.75 (mole fraction). The temperature of the solution was 75°C, and each reaction cycle was 5 h long.
(6) The samples were cleaved for observation by scanning electron microscopy (SEM) and measurement of PL spectra.

The schematic structure and SEM image of the cleaved sample are shown in Fig. 1. CdS/SiO_2 multilayers are not easily cleaved, and the boundaries of

multilayers are seen as they were disturbed further. The occupation of CdS is estimated from the ratio of the areas of CdS and air obtained from the SEM image of the cross section. TEA process repeat numbers of one and two correspond to CdS occupation of 65% and nearly 100%, respectively. We

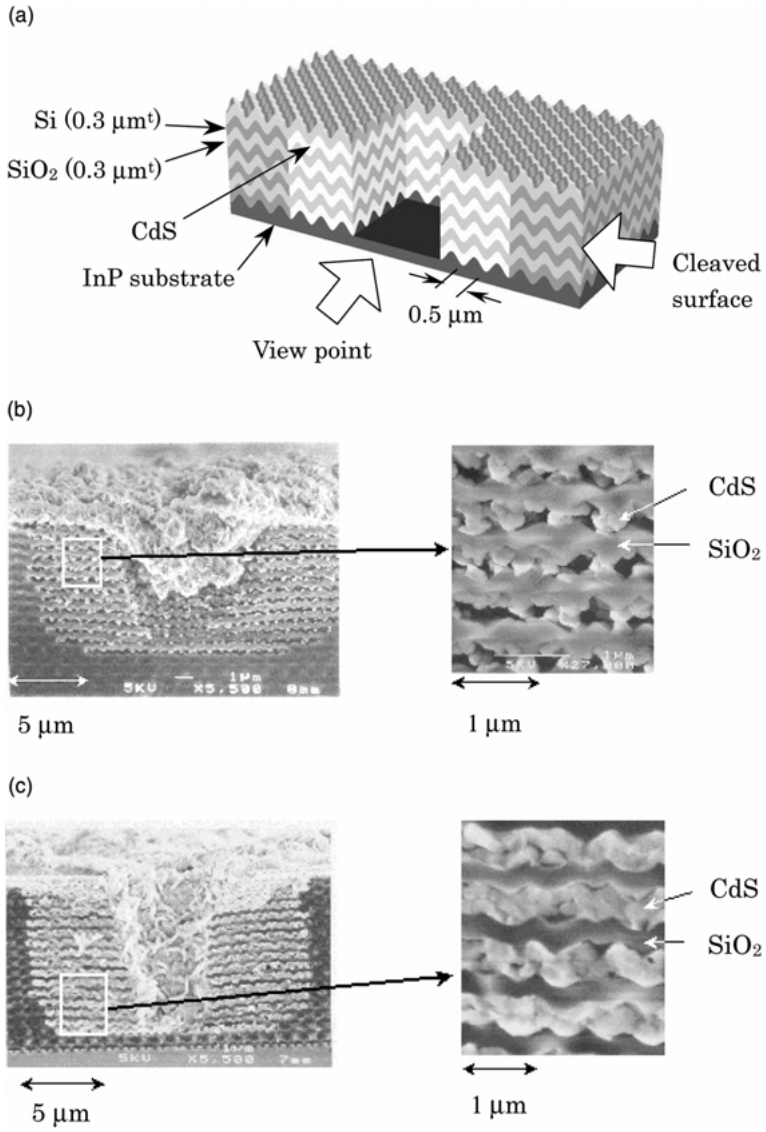

Fig. 1. Structure of the sample in which CdS is introduced in 3D PhC. (a) Schematic structure of the cleaved sample. (b) SEM pictures of the cleaved sample. Repeat number of the TEA method is one and the occupation of CdS is about 65%. (c) SEM pictures of the cleaved sample. Repeat number of the TEA method is two and the occupation of CdS is almost 100%.

found that the occupation of CdS can be controlled by regulating the repeat time of the TEA process.

2.2. OBSERVATION OF PL SPECTRA

A He–Cd laser beam (wavelength, $\lambda = 325$ nm) was used for excitation along the direction normal to the cleaved surface (spot diameter, 4 μm), and the resulting PL spectrum was observed along the direction normal to the cleaved surface. The peak wavelength and the full width of half maximum (FWHM) of the measured PL spectra were 550 and 137 nm, respectively. PL of the 3D periodic structure had almost the same spectrum as that observed for the CdS deposited on the flat glass. In this experiment, excitation and observation of the PL spectrum were only performed for the surface region of the cross section, and the effects of a PhC have not yet been observed.

3. Introducing CdS into 2D PhCs

3.1. FABRICATION PROCESS

In order to obtain a high degree of polarization dependence for the PL, we introduced CdS into 2D PhCs. The process of introducing CdS with low occupation into TiO_2/air 2D structures with a large refractive index difference was as follows:

(1) Grooves with a pitch of 0.25 μm were formed on a SiO_2 film deposited on an InP substrate, using EB lithography and dry etching.
(2) TiO_2 and SiO_2 films were laminated alternately on the grooved substrate by rf bias sputtering (10 periods). The thickness of each layer was 0.105 μm and the total thickness was 2.1 μm.
(3) Rectangular holes with dimensions $3 \times 9 \times 3$ μm^3 were formed by FIB etching.
(4) TiO_2/air periodic structures were formed with the depth of 3 μm from the walls of the rectangular holes, by selective wet etching of SiO_2, using buffered HF.
(5) CdS was introduced into the air region by the TEA method. CdS deposited on the surface of a PhC can be removed mechanically with no damage.
(6) The sample was cleaved so that the cross section containing CdS was made available for SEM observation and PL measurements.

The schematic structure of the cleaved sample is shown in Fig. 2. The occupation of CdS against the air region was estimated from the SEM image to be approximately 60%.

3.2. MEASUREMENTS OF PL SPECTRA

A He–Cd laser beam (λ = 325 nm) was focused onto the cleaved surface along the y direction to excite the introduced CdS near the substrate. The PL radiating along the z direction was collimated by a lens, passed through a polarizer, and focused again onto a monochromator.

Fig. 3 shows the measured PL spectra. The elements polarized along the x and y axes were defined as TM and TE elements, respectively. The TM element was suppressed compared to the TE element in the wavelength region of 500–660 nm, and the maximum ratio of TE/TM was approximately 2 dB (λ = 550 nm). Fig. 4 shows the transmittance along the z direction calculated using the finite difference time domain (FDTD) method. This structure was designed to function as a polarization splitter [2] at around λ = 600 nm, and the wavelength region of 550–620 nm was the passband for the TE element and the stopband for the TM element. The transmission of the light beam radiated from the lowest CdS layer was calculated, and the difference in transmission between the TE and TM modes was approximately 100% in the wavelength region of 550–620 nm. In our experiment, we irradiated a cross section containing several CdS layers with the laser beam for excitation, and observed that the polarization dependence was less than that which had been calculated. The wavelength range in which the TM element

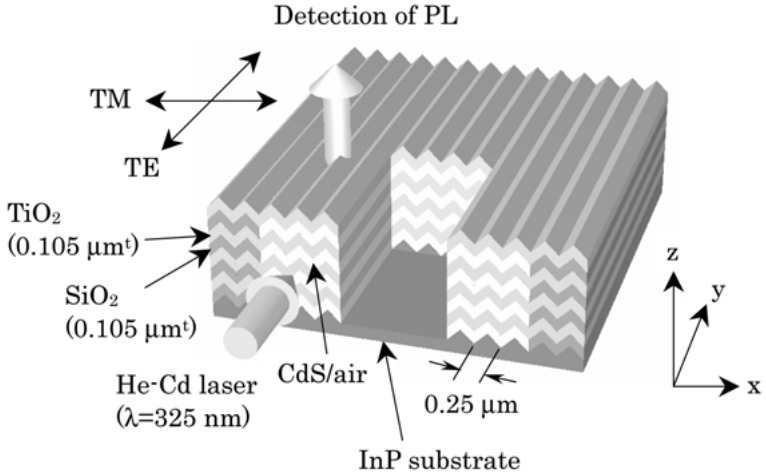

Fig. 2. Schematics of the CdS/air/TiO_2 2D PhC structure.

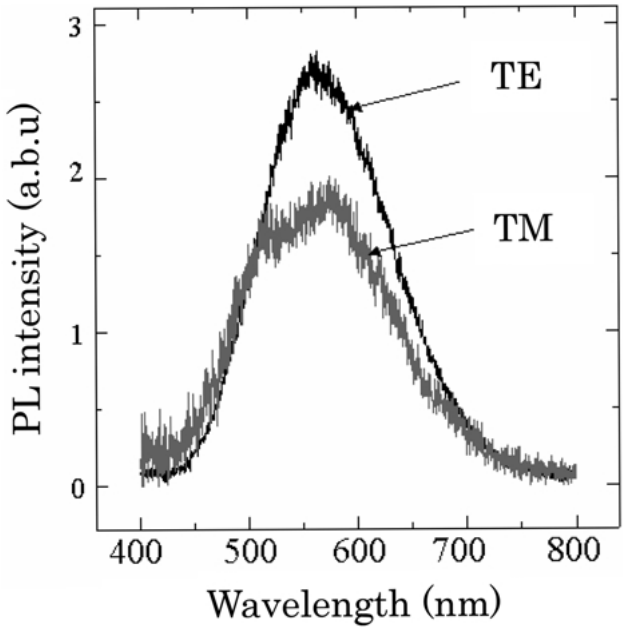

Fig. 3. Measured PL spectra of the CdS/air/TiO_2 2D PhC structure.

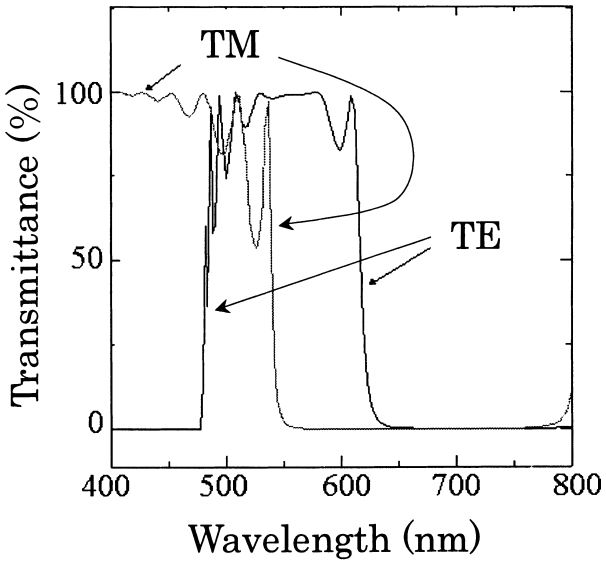

Fig. 4. Calculated transmittance in the z-direction of the CdS/air/TiO_2 2D photonic crystal structure.

was suppressed in the experiment, 500–660 nm, corresponds approximately to a calculated range of 550–620 nm.

4. Conclusion

In this study, we demonstrated a method for introducing functional materials into 2D and 3D PhCs by providing source materials in a liquid phase. Polarization dependence was observed for the PL spectra radiating normal to the surface of TiO_2/air/CdS 2D PhC structures. Our method can be used to introduce other functional materials such as particles with submicrometer diameters dispersed in liquids or polymers. The fact that CdS can be sputtered suggests that finer periodic structures can be formed by autocloning. We are currently preparing a sputtering apparatus for use in forming PhCs that contain functional materials such as CdS, using only an autocloning process.

Acknowledgments

The authors would like to thank T. Sato, T. Kawashima, K. Miura, and Y. Sakai for their help in the fabrication of samples. This study was supported by a grant-in-aid for scientific research from the Japan Society for the Promotion of Science, and special correlation funds for promoting science and technology from the Science and Technology Agency. Support was also provided by the Association for the Progress of New Chemistry (ASPRONC), and the Murata Science Foundation. This study was carried out in part at Spinics Research Center, Research Institute of Electrical Communication, Tohoku University.

References

Hanaizumi, O., Y. Ohtera, T. Sato and S. Kawakami. *Appl. Phys. Lett*. **74** 777, 1999.

Hu, H. and P. K. Nair. *J. Crystal Growth*. **152** 150, 1995.

Imada, M., S. Noda, A. Chutinan and T. Tokuda. *Appl. Phys. Lett*. **75** 316, 1999.

Inoue, K., M. Sasada, J. Kawamata, K. Sakoda and J.W. Haus. *Technical Digest of International Quantum Electronics Conference (IQEC'98)*, p. 47. San Francisco, 3–8 May. 1998.

Kawakami, S. *Electron. Lett*. **33** 1260, 1997.

Kosaka, H., T. Kawashima, A. Tomita, M. Notomi, T. Tamamura, T. Sato and S. Kawakami. *Phys. Rev. B* **58** R10096, 1998.

Meier, M., A. Mekis, A. Dodabalapur, A. Timko, R.E. Slusher, J.D. Joannopoulos and O. Nalamasu. *Appl. Phys. Lett*. **74** 7, 1999.

Ohtera, Y., T. Sato, T. Kawashima, T. Tamamura and S. Kawakami. *Electron. Lett*. **35** 1271, 1999.

Painter, O., R.K. Lee, A. Scherer, A. Yariv, J.D. O'Brian, P.D. Dapkus and I. Kim. *Science*. **284** 1819, 1999.

Romanov, S.G., A.V. Fokin, N.P. Johnson and R.M. De La Rue. *Technical Digest of International Workshop on Contemporary Photonic Technologies (CPT'98)*, p. 209. Tokyo, 12–14 Jan. 1998.

Yablonovitch, E. *Phys. Rev. Lett*. **58** 2059, 1987.

Yoshino, K., S.B. Lee, S. Tatsuhara, Y. Kawagishi, M. Ozeki and A.A. Zakhidov. *Appl. Phys. Lett*. **73** 3506, 1998.